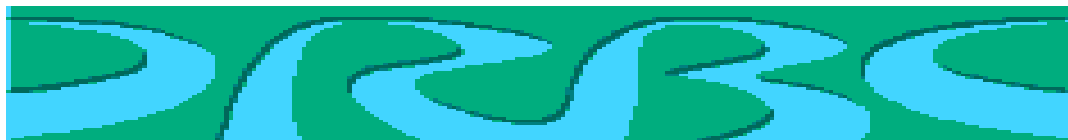


PCB WATER QUALITY MODEL FOR DELAWARE ESTUARY (DELPCB)

**DELAWARE RIVER BASIN COMMISSION
WEST TRENTON, NEW JERSEY**



Delaware River Basin Commission
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EXECUTIVE SUMMARY

Starting from July 26, 2000, with U.S. EPA Region II's and III's endorsement, the Commission acts as the lead agency in developing the Total Maximum Daily Loads (TMDLs) for PCBs in the Delaware Estuary and worked cooperatively with the signatory parties to the Delaware River Basin Compact and their agencies and affected parties. A two-staged approach has been adopted by the Commission, as recommended by an expert panel of scientists experienced with PCB modeling. In the first stage, a reliable, calibrated, scientific-based PCB model is needed to help understand the PCB behavior in the Delaware River. Based on the same constants, coefficients, and kinetics resulting from model calibration, the model is applied to develop TMDLs.

DRBC has been developing a general purpose sorbent dynamic PCB model for the Delaware River Estuary (DELPCB). DELPCB with two organic carbon (live biotic carbon [BIC] and dead particulate detrital carbon [PDC]) state variables and one inorganic solid (IS) as a pseudo-state variable linked with the one-dimensional (1-D) DYNHYD5 to enhance sorbent dynamic simulation. IS functions as a pseudo-state variable to ensure that bulk density, porosity, and burial rate of the sediment are accurately calculated at each time step. DELPCB of the Delaware River estuary is a 1-D, time variable model that includes three types of mass balances: (1) a water balance; (2) an organic carbon (OC) balance; and (3) a PCB balance. The water balance describes the influence of river flow rates and mixing rates. DELPCB treats the two OC sorbents as non-conservative state variables that are advected and dispersed among water segments, that settle to and erode from benthic segments, and that move between benthic segments through net sedimentation or erosion. The sediment process of DELPCB is a simplified version of the sediment process model that includes (1) depositional flux of OC (PDC), (2) degradation of such flux (PDC), and (3) the resulting sediment (PDC) flux. The PCB mass balance tracks all sources, losses and internal transformations of PCBs in the river. During the modeling process, upon receiving the information of physical transport from DYNHYD5, DELPCB simulates the spatial and temporal distributions of water quality parameters such as BIC, PDC, total PCB, particulate PCB, and truly dissolved PCB, and DOC-bound PCB. PCBs are then transported and transformed by dispersion, pore water diffusion, organic carbon motion, and volatilization. The water quality model consists of 87 water column segments, 87 surface sediment segments, 87 layer 2 sediment segments, and 87 layer 3 (bottom layer) sediment segments. These segments are interconnected. A 5-cm surface sediment layer (considered as an active layer) underlies each of the water column segments of the Delaware River Estuary. A 5-cm layer 2 underlies the surface layer segments and a 30-cm layer 3 underlies the layer 2 segments. DELPCB is a homolog-base model. In this study, we examine and evaluate the fate and transport of penta PCB. All data are evaluated and calculated based on weighted average of penta PCB congeners.

Finally, DELPCB is a simulation program enhanced from EPA's Water Quality Simulation Program (WASP) Version 5.12. The enhancements or added features to WASP5 includes (1) OC decay in both water column and sediment; (2) constantly maintained PDC to IS ratio and porosity during the surface sediment burying process; (3) spatial and temporal varying DOC concentrations; (4) independent values between PCB partitioning coefficients to DOC and OC; (5) temperature dependent Henry's Law constant; (6) spatial and temporal varying gaseous PCB, and air-water flux conversions; and (7) new formulation for volatilization mass transfer coefficient (k_v). This report documents the water quality model including formulations of the kinetic processes and sediment processes.

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1 INTRODUCTION

1.1 PROJECT TASKS, PRODUCTS, AND COMPLETION TIMETABLE

The Delaware River PCB modeling study is composed of two major tasks:

Modeling Framework Development—This task includes developing the objective and scope of the modeling study; evaluating data availability; examining data collection needs; developing the conceptual model of the system; assessing and selecting the models to use; describing the modeling approach; and proposing/defining model calibration procedures.

Performance of the Modeling Studies—This effort consists of development and application of the Delaware River PCB model in a phased approach consistent with the modeling study's design objectives. Required efforts include data collection, model setup, and model calibration for the hydrodynamic and water quality submodels.

1.2 PRODUCTS AND COMPLETION TIMETABLE

The first generation PCB model (including water quality and hydrodynamic model) is scheduled for completion in September 2003. The follow-up second generation PCB model development will be continued upon completing the technical review of the first generation PCB model. This project is scheduled with the following products:

First generation PCB model and interim report (9/2003)

Presentation at the National Conference on PCB modeling (Spring/2004)

1.3 OVERVIEW

DRBC has been developing a general purpose sorbent dynamic PCB (SDPCB) model for the Delaware River Estuary (DELPCB). DELPCB with two organic carbon state variables and one inorganic solid (IS) as a pseudo-state variable linked with the one-dimensional (1-D) DYNHYD5 to enhance sorbent dynamic simulation. IS functions as a pseudo-state variable to ensure that bulk density, porosity, and burial rate of the sediment are accurately calculated at each time step. The model generates additional IS based on depositional OC assuming the OC/IS ratio remains constant. The sum of IS and OC (or PDC) burial rate computed by DELPCB represents sediment burial rate and is compared with sediment core data (see Section 2.4.2 for details).

Biotic carbon (BIC, live organic carbon) and particulate detrital carbon (PDC, dead organic carbon) are two organic carbon (OC) sorbents treated as state variables in the model. PCB, partitioning into particulate- PCB, truly dissolved-PCB, and dissolved organic carbon (DOC) bound-PCB phases, transported with OC is treated as one state variable. The real time model simulates tidal flows, spatial and temporal distributions of OC and PCB.

DELPCB is a simulation program enhanced from EPA's Water Quality Simulation Program (WASP) Version 5.12 (Ambrose et al. 1993). The enhancements or added features to WASP5 are summarized as follows:

- OC decay in both water column and sediment;
- Constantly maintained PDC to IS ratio and porosity during the surface sediment burying process;
- Spatial and temporal varying DOC concentrations;
- Independent values between PCB partitioning coefficients to DOC and OC;
- Temperature dependent Henry's Law constant;
- Spatial and temporal varying gaseous PCB, and air-water flux conversions; and
- New formulation for Volatilization Mass Transfer Coefficient (k_v).

DELPCB is a homolog-base model. In this study, we examine and evaluate the fate and transport of penta PCB. All data are evaluated and calculated based on weighted average of penta PCB congeners.

DELPCB treats the two OC sorbents as non-conservative state variables that are advected and dispersed among water segments, that settle to and erode from benthic segments, and that move between benthic segments through net sedimentation or erosion. Mass balance computations are performed in benthic compartments as well as water column compartments. Bulk densities or benthic volumes are constantly maintained for surface sediment throughout the simulation. Such OC settle through the water column and deposit to underlying benthic segments at user-specified deposition velocities and return at resuspension velocities that may vary both in time and in space. The sediment process of DELPCB is a simplified version of the sediment process model that includes three basic processes:

- Depositional flux of OC (PDC),
- Degradation of such flux (PDC), and
- Resulting sediment (PDC) flux.

Upon receiving the OC from the overlying water column, DELPCB simulates their degradation process (by specifying appropriate decay rates), resulting fluxes of OC (by mass balance calculations), and sediment oxygen demand (SOD) back to the water column (by specifying appropriate diffusion rates). Sediment PDC degradation rate of 0.00026/day used in DELPCB is consistent with measured/calibrated SOD rates and an oxygen:carbon ratio (32/12), with the assumption that the SOD exertion (due to diagenesis) occurs in the surficial sediment layer (HQI 1995, Gelda et al. 1995). The influence of the sediment water column coupling activities are more pronounced in the long term change of PCB concentrations in response to changes in PCB loads (see DRBCC for details). This report documents the water quality model including formulations of the kinetic processes and sediment processes.

2 CONCEPTUAL APPROACH

2.1 BACKGROUND

For water quality management purposes, Zone 2 begins at RM 133.4 and stretches to RM 108.4. Zone 3 begins at RM 108.4 and ends at RM 95.0. Zone 4 starts from RM 95.0 and ends at RM 78.8. Zone 5 covers the areas between RM 78.8 and RM 48.2. Zone 6 includes the areas between RM 48.2 and RM 0.0 .

2.2 MODELING OBJECTIVES

In the first stage, a reliable, calibrated, scientific-based PCB model is needed to help understand the PCB behavior in the Delaware River. Such a model not only allows us to conduct a detailed quantitative evaluation of the sources, inventories, concentrations, and effects of PCBs but also addresses the relationship between sources of PCBs and concentrations in air, water, and sediment in the Delaware River. Important activities such as load estimation (including OC and PCBs from both air and water) and ambient monitoring efforts are put together in a modeling framework. Estimated loads that transport into and out of the Delaware River and distribute between water column and sediment are computed in the modeling framework. Based on these estimates and computation, the model can determine the rate of change in concentrations and system response to the change of PCBs sources, e.g., tributary loadings or air influxes or volatilization. Based on the same constants, coefficients, and kinetics resulting from model calibration, the model is applied to develop TMDLs.

The modeling efforts should meet the following five objectives:

Provide a reliable modeling framework for integrating load estimates and ambient data.
Calibrate PCB model using ambient data collected from different flow regimes, based on models for hydrodynamic, OC sediment transport, and PCB fate and transport.
Based on the model simulation, evaluate the magnitude and variability of PCB fluxes between air, water column, and sediment.
Identify further monitoring and modeling efforts to address additional PCB sources and reduce the uncertainty of PCB predictions.
Upon calibrated, the PCB model is applied to TMDLs development based on the same constants, coefficients, and kinetics resulting from model calibration.

2.3 MODELING FRAMEWORK

To meet the above-mentioned objectives, a comprehensive and integrated assessment of the hydrodynamic, sediment processes, and PCB fate and transport in the Delaware River is required to developed because no single model adequately represents the processes of PCB in the River. Thus, there are needs for selecting and running separate hydrodynamic and water quality submodels; and implement (or establish) appropriate linkage between these submodels. The following section discusses existing water quality and hydrodynamic models for the Delaware estuary.

2.3.1 Existing Water Quality and Hydrodynamic Models for the Delaware Estuary and Current Needs

A one dimensional (1-D) DELTOX model, consisting of 79 water columns and 11 tributaries of the Delaware River has been established by the DRBC to address volatile organic chemicals in the Delaware River (DRBC 1998). The physical domain (water quality segments) for DELTOX model covers Delaware River at Trenton (RM 133.4) to Liston Point (RM 48.0) instead of covering Delaware River at Trenton (RM 133.4) to near mouth of Bay (RM 6.0) so the model needed expansion and resegmentation. Furthermore, a calibrated model of the Delaware River for PCBs needed to be developed in order to establish numerical values for the TMDL in each of four zones of the river, and determine waste load allocations for significant point sources and load allocations for significant non-point sources. The model needed to be a fine grid, time variable model which includes at least two major components: a hydrodynamic model and water quality model (including sediment transport mechanisms). Also the water quality model needed to be run sequentially with the hydrodynamic model. The water quality model needed to be developed to accept the loadings from the various source categories, partition the PCBs between various phases (e.g., dissolved, DOC-bound, particulate), and apply degradation processes for OC instead of PCB. We assume no PCB decay.

The modeling framework is composed of the following two component models:

U.S. EPA Water Quality Simulation Program Version 5.12 (WASP5)/TOXI5 —Water Quality/ Sediment Transport Model

U.S. EPA The Dynamic Estuary Model, Hydrodynamic Program, DYNHYD5 (1-D)

2.3.2 Using WASP5/TOXI5 As the Engine in Water Quality Model and Code Modifications to WASP5/TOXI5

WASP5 was selected as the water quality model as per recommendation from PCB modeling expert panel. There are numerous successful modeling projects in the nation that used WASP5 as simulation engines. Among those projects, Everglades Screening Study Project (Ambrose 1996), Hudson River PCBs Modeling/Reassessment RI/FS (EPA 2000a), and Lake Michigan Mass Balance Project (2000b) are most significant, highly visible WASP related project in the recent years. Among these three projects, Hudson River PCBs Modeling/Reassessment RI/FS has a similar modeling physical domain as those of Delaware River. Experiences learned from the Hudson River study should be useful for our study. However, results from DRBC's monitoring programs indicate that the major PCB sources to the Delaware River Estuary are mainly from the external loads (point, nonpoint discharges, and air influxes) instead of those from the sediment in Hudson River. With such significant differences between these two studies, an independent modeling effort was required due to the unique characteristic of PCB sources in the Delaware River.

Upon examining the algorithms of standard WASP5/ TOXI5 (hereafter referred as TOXI5), its three types of "solids" the state variables are conservative, which indicates that no existing kinetics functions are available or applicable between solids. Even though the fraction of OC to solid can be assigned to each solid type to compute its corresponding OC,

without appropriate code modifications or enhancement, standard TOXI5 does not mass balance OC, which should include live (BIC), detrital (PDC), and the remaining non-organic carbon fraction (IS). As per recommendation/guidance from PCB modeling expert panel, the scope of enhancement to TOXI5 includes:

2.3.2.1 OC decay in both water column and sediment

To develop a good OC sorbent dynamic model (OCSD), decay rates need to apply to both BIC and PDC. Such an OCSD model should apply water column gross settling and decay functions to describe physical and biological processes for BIC and PDC. Within the water column, BIC is converted to PDC and then transformed into DOC. In the sediment layer, PDC decays into BIC. The decay rate was estimated from sediment oxygen demand (SOD).

2.3.2.2 Constantly maintained PDC to IS ratio and porosity during the surface sediment burying process.

For variable bed volume (or constant density) option, surface layer should maintain a constant density for PDC, IS, and their ratio; and thus porosity should be constantly maintained.

2.3.2.3 Spatial and temporal varying DOC concentrations

It is recommended that model treat DOC as a parameter (i.e., its values are assigned or inputted externally) not as a state variable. In standard TOXI5's input options, DOC can be incorporated as spatial variables in Group G: Parameter but is not a temporal variable. The enhancement of temporal varying DOC is required. Such enhancement allows the temporal flexibility of DOC in the model. Data from the Delaware Estuary show temporal and spatial variability of DOC. (J. Sharp, personal communication)

2.3.2.4 Independent values between PCB partitioning coefficients to DOC and OC

In standard TOXI5, there is only one PCB partitioning coefficient to OC (K_{oc}) but no other value can be assigned to PCB partitioning coefficient DOC (K_{doc}). As indicated in the literature, binding capacity of PCBs with POC is greater than that observed with DOC in Great Lakes waters (i.e., K_{oc} is greater than K_{doc}) (Gilek et al., 1996) (Strange and Swackhamer, 1994) (as referred to as Chapra, 1997). It is suggested by PCB modeling expert panel that a value of K_{doc} that is 10 percent of the value for K_{oc} .

2.3.2.5 Temperature dependent Henry's Law constant

Congener-specific Henry's (H) constants reported by Dunnivant et al, 1992 are used to calculate Henry's constant for each PCB homolog. After applying Gas Law conversion factors, the value for the dimensionless Henry's constant (H') for each PCB homolog is calculated. For the penta-PCB homolog, H' and molecular weight was calculated by weight of average of congener distribution. As suggested by the PCB modeling expert

panel, newly developed empirical formulas for temperature dependent H' by Bamford et al. 2002 are incorporated into the model.

2.3.2.6 Spatial and temporal varying gaseous PCB, and air-water flux conversions.

The concentration of PCB in air (c_{air}), expressed in term of atmospheric (gaseous) PCB concentration (ATMOS) in the standard TOXI5, is programmed as a constant, which is neither spatially nor temporally variable. From DRBC's Air/Water Flux study results (preliminary), c_{air} varied from reach to reach (spatial variation) in the Delaware River with temperature variation. To better describe the field conditions in the river, we need to modify current standard TOXI5 for c_{air} accordingly. It was suggested by PCB modeling expert panel that empirical formulas be spatially specific and temperature dependent c_{air} resulting from DRBC's sampling programs and derived by Totten et al. 2003 are incorporated into the model.

2.3.2.7 New formulation for Volatilization Mass Transfer Coefficient (k_v)

The mass transfer coefficient is dependent on the rates of mass transfer through relatively thin layers of water and air at the interface, which are in turn dependent on the concentration gradients in the layers, and the temperature-dependent diffusivity of PCBs in the layers: In standard TOXI5, k_v can be both temporally and spatially variable by using the combination of volatilization option 4 for XV, multiplier of time function 5, REAER, and time variable reaeration coefficient, REARN as well as air temperature, AIRTMPN to get K_a (reaeration rate). A good air-water formulation for the estuary should include both tidal velocity and wind-driven effects for tidal systems. We have reviewed the tidal velocity formulas, e.g., O'Connor-Dobbins (1958), Churchill (1962), Ovens-Gibbs (1964) for streams and rivers; and wind-driven effects, e.g., Broecker et al. (1978), Wanninkhof et al. (1991), Banks and Herrera (1977), and O'Connor (1983) for lakes. DELPCB incorporates Thomann and Fitzpatrick (1982) equation, which combines O'Connor-Dobbins and Banks and Herrera (1977). The idea of adopting Thomann and Fitzpatrick (1982)'s equation is that such an equation provided a straight forward description of both tidal velocity and wind-driven effects for tidal systems in a continuous format. Time variable reaeration rate, K_a equals $K_L O_2$ (mass transfer coefficient of oxygen for the liquid laminar layer) divided by H (mean depth). We then convert $K_L O_2$ to K_L . PCB (mass transfer coefficient of PCB for the liquid laminar layer) via a molecular weight function described by Mills et al. (1982). For the gas-film coefficient of water (K_{gH_2O}), Mills et al (1982) also illustrated wind-base equation. Similar approach can be applied to covert such coefficient from water to PCB.

Detailed discussions on code modifications or enhancement to WASP5/TOXI5 can be found in the Appendix.

2.3.3 General Description of DYNHYD5 (1-D) and Code Modifications To DYNHYD5

Please see Hydrodynamic Report (2003a) for details.

2.4 OVERVIEW OF MODELING APPROACH

DELPCB, enhanced from TOXI5 is a general dynamic mass balance framework for modeling contaminant fate and transport in surface waters. A body of water is represented in DELPCB as a series of discrete computational elements or segments. Environmental properties and PCB concentrations are modeled as spatially constant within segments. Each state variable (such as BIC, PDC) is advected and dispersed among water segments, and exchanged with surficial benthic segments by diffusive mixing. Sorbed or particulate fractions may settle through water column segments and deposit to or erode from surficial benthic segments. Within the bed, dissolved variables may migrate downward or upward through percolation and pore water diffusion. Sorbed variables may migrate downward or upward through net sedimentation or erosion. DELPCB, allows applying water column gross settling and decay functions to describe physical and biological processes for BIC and PDC. All the processes are described by rate equations (see Kinetic Equation Section). Rate equations are quantified either by first-order constants or by second-order constants and environment-specific parameters that may vary in space and time.

DELPCB simulates the transport and transformation of one PCB homolog (penta-PCB), two OCs (live OC as BIC and detrital OC as PDC), and one solid (IS as non-organic carbon). PCB can exist in four phases (particulate-PCB, DOC bound-PCB, dissolved-PCB, and gaseous-PCB). Local equilibrium is assumed so that the distribution of the PCB between phases is defined by distribution or partition coefficients. The model, then, is composed of four systems, one PCB, two OCs, and one solid, for which the mass balance equations (see Mass Balance Equation Section) are solved.

In an aquatic environment PCB may be transferred between phases and may be degraded by any of a number of chemical and biological processes. Transfer processes defined in the model include sorption and volatilization. Transformation process defined includes biodegradation. Sorption is treated as an equilibrium reaction. All the processes are described by rate equations (see Kinetic Equation Section). Rate equations are quantified either by first-order constants or by second-order constants and environment-specific parameters that may vary in space and time. In this modeling effort, we focus on penta-PCB homolog and assume no biodegradation (decay) for such homolog.

2.4.1 Physical Domain And Model Segmentation

DELPCB of the Delaware River estuary is a 1-D, time variable model that includes three types of mass balances: (1) a water balance; (2) an OC balance; and (3) a PCB balance. The water balance describes the influence of river flow rates and mixing rates. The OC balance describes the dynamics influencing PCB sorbed to both suspended and bedded OC. The PCB mass balance tracks all sources, losses and internal transformations of PCBs in the river.

DELPCB is an application of EPA WASP toxic chemical model WASP5/TOXI5. The most efficient (both time and cost) way of running the model is to perform model runs using the maximum stable time step. This can be done by appropriate segmentation techniques. To achieve maximum stable time step of the model, at each segment, the advected, dispersed, and transformed mass must be less than the resident mass. Another

important step for assigning an appropriate time step is to minimize numerical dispersion, which is an artificial mixing introduced by term of dispersion while assigning a small time step. To avoid such a pitfall, it is important to use a time step somewhat less than resident time equal to V (segment volume)/ Q (flow)

The water quality model consists of 87 water column segments, 87 surface sediment segments, 87 layer 2 sediment segments, and 87 layer 3 (bottom layer) sediment segments. These segments are interconnected. A 5-cm surface sediment layer (considered as an active layer) underlies each of the water column segments of the Delaware River Estuary. A 5-cm layer 2 underlies the surface layer segments and a 30-cm layer 3 underlies the layer 2 segments (see Figures 1a and 1b).

Modeling framework boundaries for hydrodynamic model (DYNHYD5) and water quality model (WASP5/TOXI5) covers Delaware River at Trenton (RM 133.4) to mouth of Bay (RM 0.0). The linkage between the two models is illustrated in Figure 2.

Figure 1a - Map of Model Segmentation

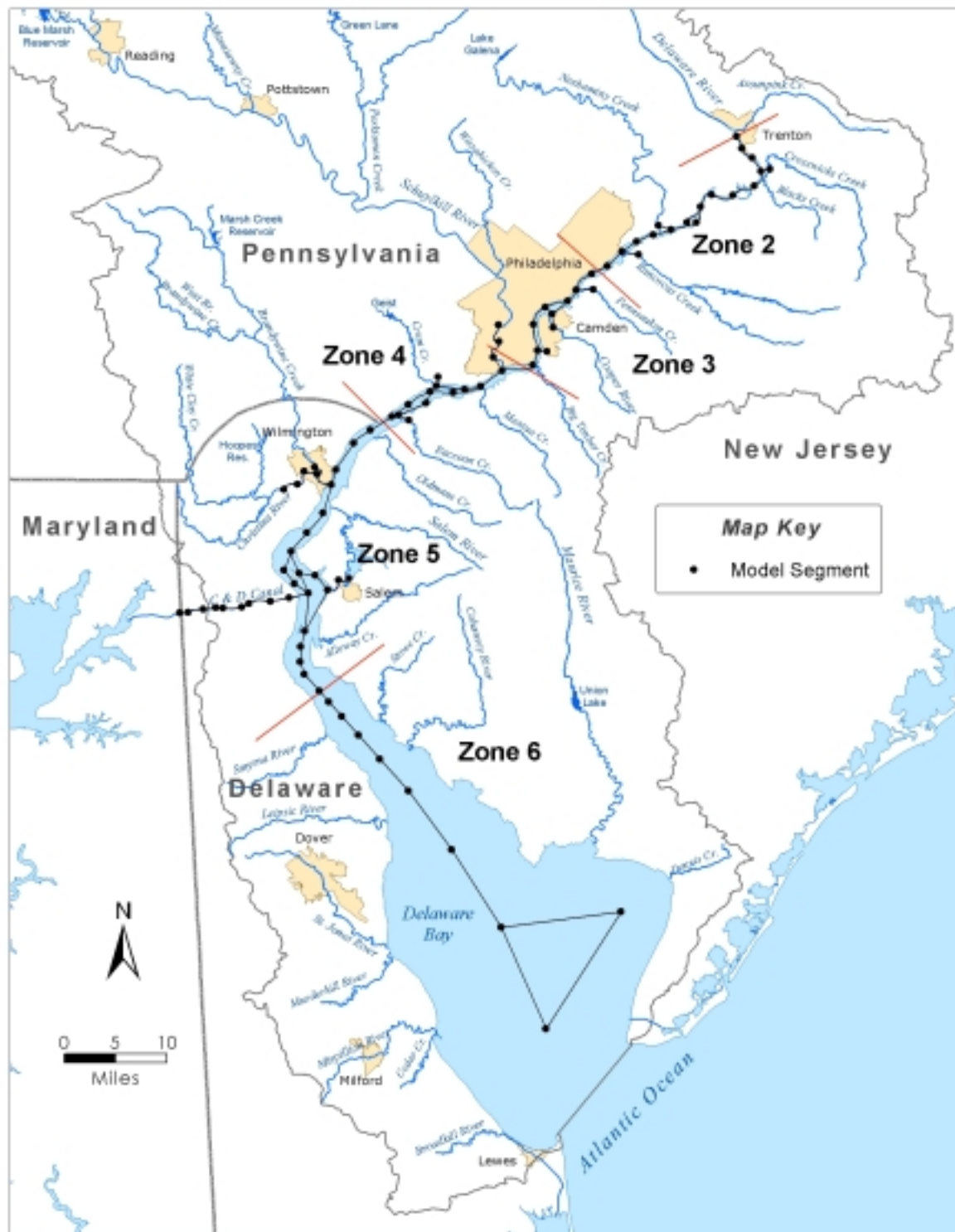


Figure 1b - Schematic Diagram of Model Segmentation

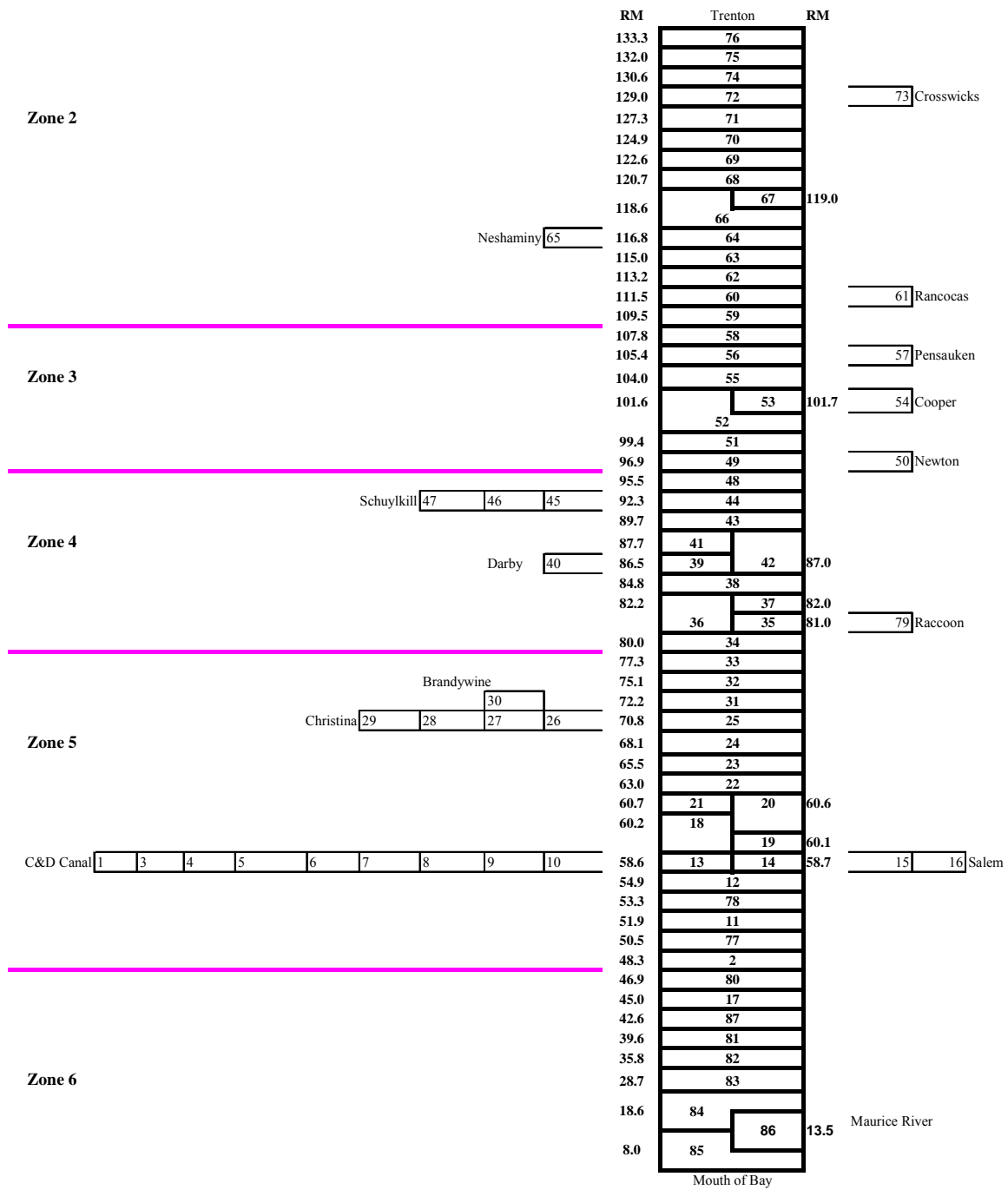
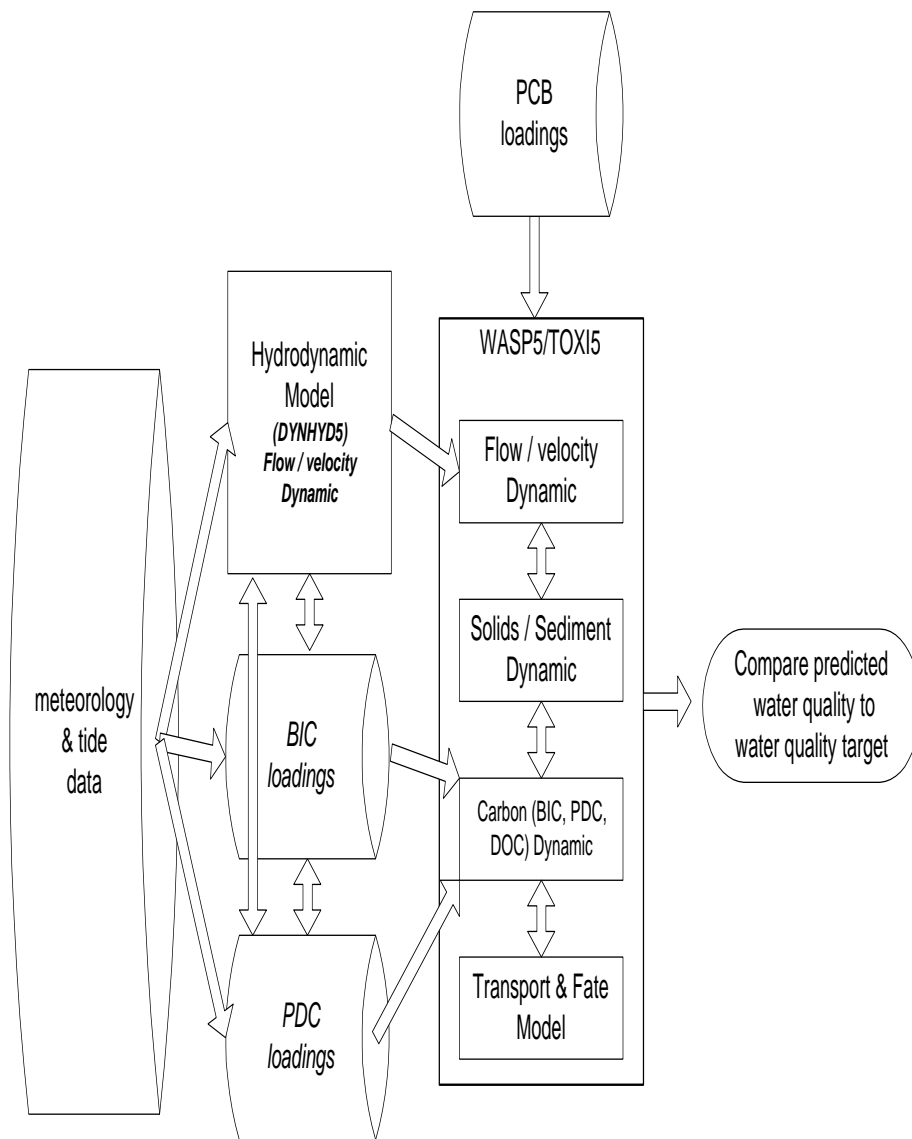


Figure 2 PCB Conceptual Modeling Framework



2.4.2 OC Sorbent Dynamic

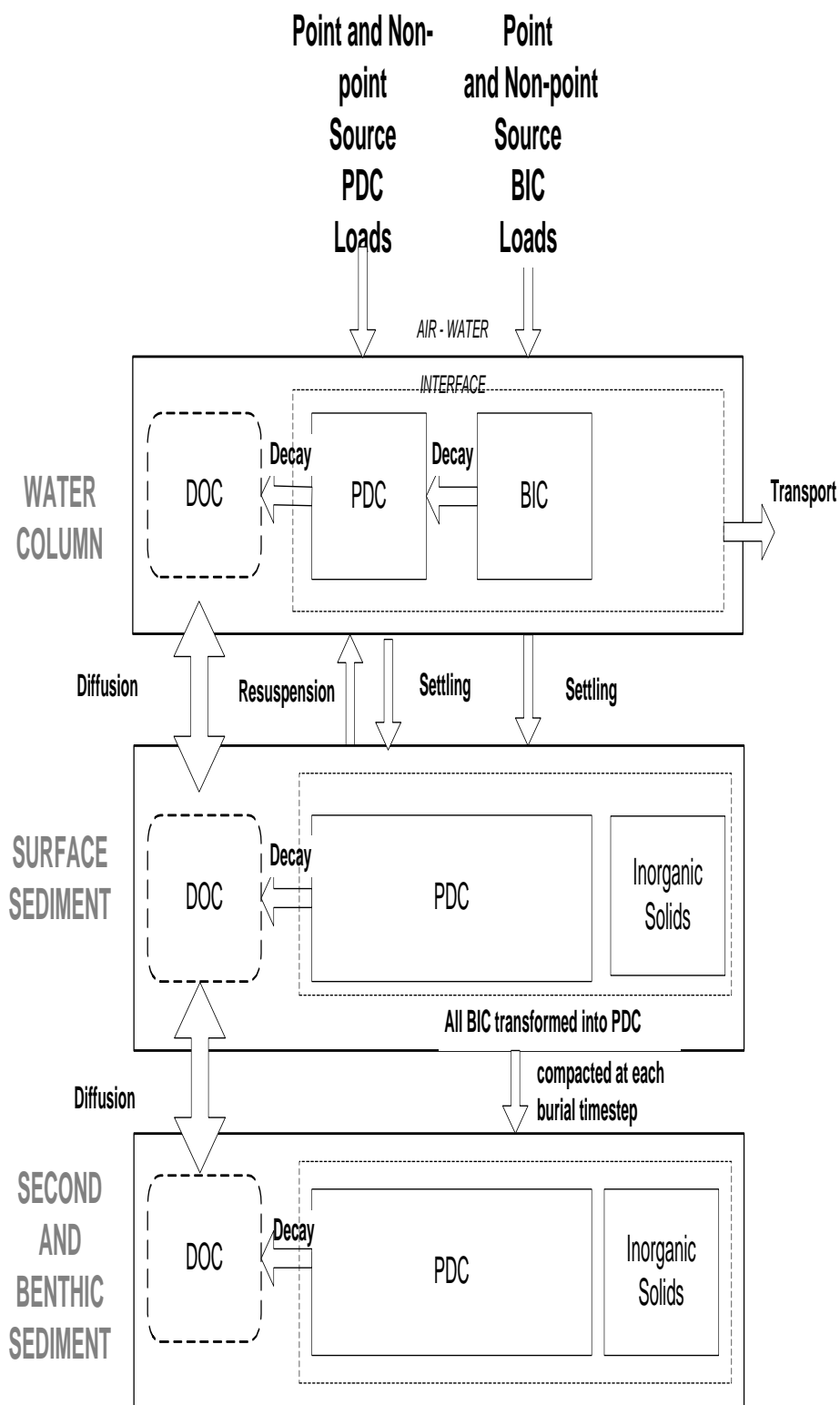
The PCB model for Delaware River Estuary is a carbon-base sorbent dynamic transport model with water column gross settling and decay functions for BIC and PDC (see Figure 3). Within water column, BIC is converted to PDC at the rate of 0.2/day and then, transformed into DOC at the rate of 0.05/day. Upon settling to the sediment, all BIC turns into PDC and is then resuspended or buried. PDC in the sediment has a decay rate of $5E-5$ /day. There are three sediment layers: surface layer (layer 1), intermediate layer (layer 2), and bottom layer (layer 3). The first two layers are 5 cm deep and the third layer 30 cm deep. The selection of surface layer depth of 5 cm is based on: (1) available sediment data, mostly surface grabs representing a 5 cm surface layer; and (2) interpretation of dated sediment core profiles. An inorganic solid (IS) is coexistent with PDC for all three sediment layers. IS does not exist in the water column and is not resuspended with PDC from the sediment, but is buried with PDC. A sediment burial time step of 73 days is assigned to the model.

In DELPCB, the movement of sediment in the bed is governed by the variable bed volume option, which maintains total organic carbon concentration in the bed constant. This allows bed volumes to change in response to deposition and scour. Two types of bed layers are assumed: an upper uncompacted layer (layer 1) and one (layer 2) or more lower (layer 3), more compacted layers. When deposition exceeds scour, the upper layer increases in volume as the surface of the bed rises. After a period of time, the added volume of upper bed compresses and becomes part of the lower bed. When scour exceeds deposition, the volume of the upper layer decreases as the surface of the bed drops. When the upper layer erodes completely, the next layer of bed is exposed to scour. The model uses an explicit one-step Euler solution technique. As such, there is potential for instability or numerical dispersion in the user-specified computational network. These problems can usually be controlled acceptably by manipulating the time step.

PCB is transported with OC. However, IS does coexist with OC in the sediment. Such implementation is reasonable because the real bulk density and porosity of the sediment must be accurately calculated at each time step so that the sediment process can be correctly simulated. IS is also an important indicator for burial rate calculations. During the sediment burying process there is no depositional IS flux from water column. The model generates additional IS based on depositional OC assuming the OC/IS ratio remains constant. These additional IS is buried with OC to maintain the same OC/IS ratio and bulk density. The sum of IS and OC (or PDC) burial rate computed by DELPCB represents sediment burial rate and is compared with sediment core data. IS is included as a pseudo state variable in the sediment to maintain accurate bulk volume, which was an important parameter for the long-term consistency check, while the magnitude of burial rate, changes of the bulk volume (or density) and OC to IS ratio may be an issue, if not handled properly, during the sediment process. To address bioturbation behavior, particle mixing and additional diffusion are implemented between layer 1 and 2 to enhance the interactions.

Figure 3 - Organic Carbon Processes in the Transport and Fate Model

Figure 3. Organic Carbon Processes in the Transport and Fate Model



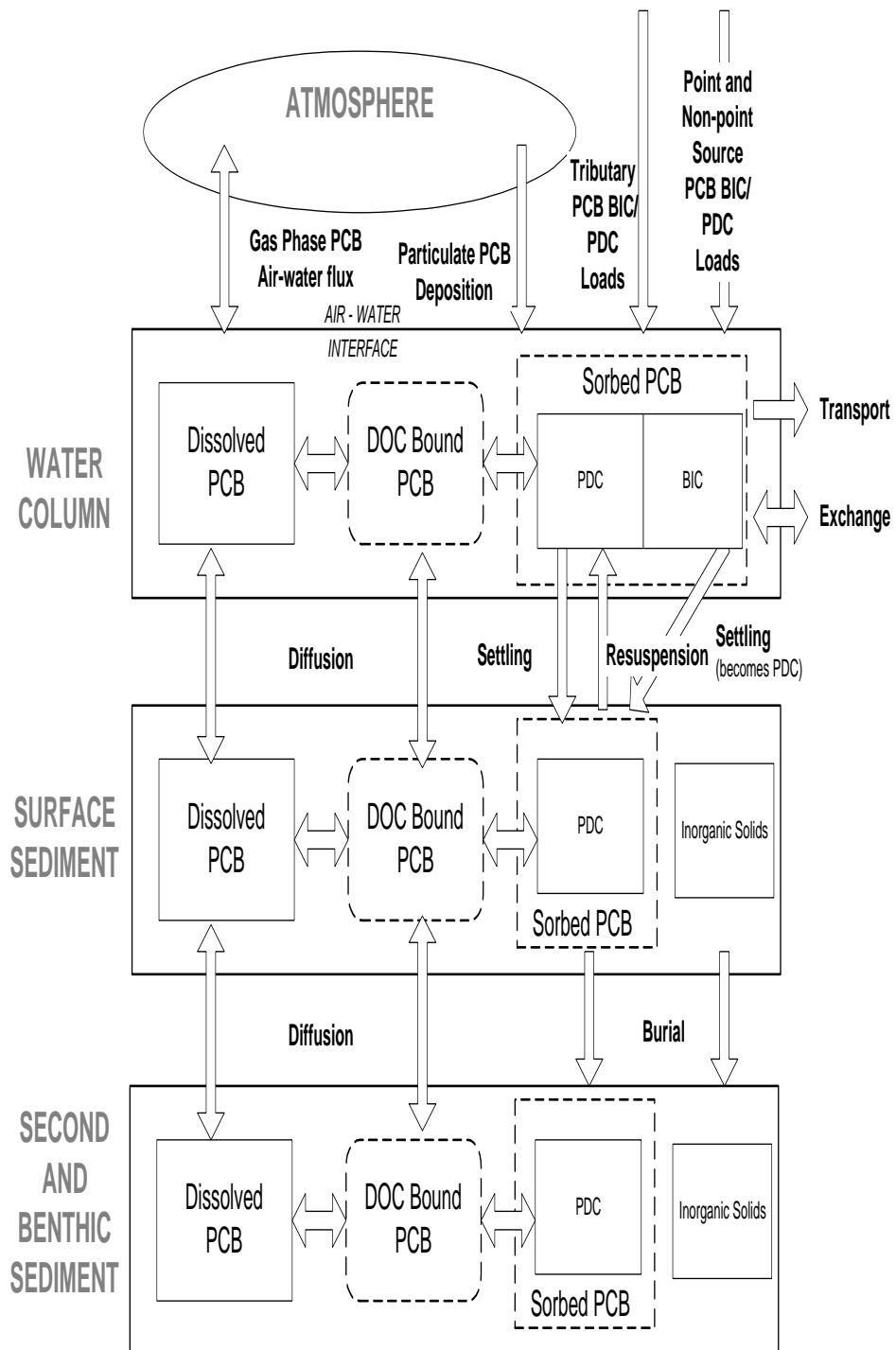
2.4.3 PCB Dynamics

The PCB mass balance tracks all sources, losses and internal transformations of PCBs in the river. Through a series of partitioning processes, PCBs partition into particulate- PCB, truly dissolved-PCB, and DOC bound-PCB phases and is then transported with OC. During the modeling process, upon receiving the information of physical transport from DYNHYD5, DELPCB simulates the spatial and temporal distributions of water quality parameters such as BIC, PDC, total PCB (TPCB), particulate PCB (PPCB), and truly dissolved PCB (DPCB), and DOC-bound PCB (DOCPCB) (see Figure 4). The sum of the latter two is abbreviated as DDPCB. PCBs are then transported and transformed by dispersion, pore water diffusion, organic carbon motion, and volatilization. The physical transport of water column OC and PCBs is governed by advective flow and dispersive mixing in the water column. The model should include all ten PCB homologs depending on the presence of the homolog. They are chlorobiphenyls with one (mono), two (di), three (tri), four (tetra), five (penta), six (hexa), seven (hepta), eight (octa), nine (nona), and ten (deca) chlorine atoms. Each homolog group exhibits significantly different behavior in terms of fate and transport (such as partition and volatilization, decay) and bioaccumulation (such as uptake, depuration, and chemical assimilation).

Because of the complex coupling between the transport and fate of particulate matter and the transport and fate of contaminants, an accurate simulation of the transport and fate of OC is critical for developing better understandings of the transport and fate of PCBs in the Delaware River. The reliability of the sediment transport component of the model is mainly dependent on the ability of the hydrodynamic model to accurately reproduce the processes of physical transport and mixing. With such accurate transport and mixing input, we can correctly simulate settling, deposition, and resuspension of suspended sediment material and of contaminants sorbed to the OC. PCBs tend to sorb to organic carbons which consist of three distinct forms, namely, biotic (live) carbon (BIC), particulate detrital (dead) carbon (PDC), and dissolved organic carbon (DOC). Particulate-bound PCB (PPCB) is transported with BIC and PDC assuming 100% carbon for both OC types. Since DOC is specified as a parameter, DOC-bound PCB (DOCPCB) is transported with DPCB via pore water diffusion.

Figure 4 - PCB and Organic Carbon Processes in the Transport and Fate Model

Figure 4. PCB and Organic Carbon Processes in the Transport and Fate Model



3 GOVERNING EQUATIONS FOR WATER QUALITY STATE VARIABLES

3.1 MASS-BALANCE EQUATIONS

3.1.1 PCB Mass Balance Equation

The governing mass-balance equation for water quality state variables PCB (Equation 1) consists of physical transport, advective and diffusive, and kinetic processes.

$$\frac{\partial C_T}{\partial t} = -u \frac{\partial C_T}{\partial x} + \frac{\partial}{\partial x} \left(E \frac{\partial C_T}{\partial x} \right) + S_D + S_R - S_V - S_S \quad [1]$$

where t is time, x is distance along the main axis of the river. C_T is the total PCBs concentration (M/L^3), E is a tidal dispersion coefficient (L^2/T), u is the average cross-sectional river velocity (L/T), S represents the sources and sinks ($M/(L^3 \times T)$) due to transfer from sediment pore water (S_D) resuspension of bed sediment (S_R), settling from water column to bed sediment (S_S), and volatilization (S_V).

3.1.2 PDC Mass Balance Equation

For another state variable PDC, due to its solid nature, there are no transfer from sediment pore water (S_D) and volatilization (S_V). The mass balance equation is reduced to:

$$\frac{\partial C_T}{\partial t} = -u \frac{\partial C_T}{\partial x} + \frac{\partial}{\partial x} \left(E \frac{\partial C_T}{\partial x} \right) + S_R - S_S \quad [2]$$

where C_T is the PDC concentration (M/L^3).

3.1.3 BIC Mass Balance Equation

For BIC, due to its biotic and solid nature, there are no transfer from resuspension of bed sediment (S_R), sediment pore water (S_D) and volatilization (S_V). The mass balance equation is further reduced to:

$$\frac{\partial C_T}{\partial t} = -u \frac{\partial C_T}{\partial x} + \frac{\partial}{\partial x} \left(E \frac{\partial C_T}{\partial x} \right) - S_S \quad [3]$$

where C_T is the BIC concentration (M/L^3).

3.1.4 IS Mass Balance Equation

Model does not include IS in the water column so its concentration remains zero. There are no transfer from sediment pore water (S_D) resuspension of bed sediment (S_R), settling from water column to bed sediment (S_S), and volatilization (S_V). IS plays an important role in the sediment process.

While solving the above-mentioned differential equations (1,2 and 3), the kinetic terms are decoupled from the physical transport terms. The mass-balance equation for physical transport only, which takes the same form as the salt-balance equation is:

$$\frac{\partial C_T}{\partial t} = -u \frac{\partial C_T}{\partial x} + \frac{\partial}{\partial x} \left(E \frac{\partial C_T}{\partial x} \right) \quad [4]$$

The equations for kinetic processes are expressed as

$$\frac{\partial C_T}{\partial t} = K C_T - S \quad [5]$$

where C_T is the state variable concentration (M/L³), K is kinetic rate constant (1/T), and S represents the sources and sinks (M/(L³ x T)).

3.2 KINETIC EQUATIONS

Model has three state variables and one pseudo state variable. This section describes the kinetic equations for each of the state variables.

- | | |
|---------|---------|
| (1) PCB | (2) PDC |
| (3) BIC | (4) IS* |

Where * represents a pseudo state variable.

3.2.1 PCB Kinetic Equations

The relationships between total, dissolved PCB (C_d), DOC-bound PCB (C_{doc}), particulate- (or organic carbon-) bound-PCB (C_p) concentrations are

$$C_d = f_d \times C_T \quad [7]$$

$$C_{doc} = f_{doc} \times C_T \quad [8]$$

$$C_p = f_p \times C_T \quad [9]$$

where f_d is fraction dissolved, f_{doc} is fraction of doc, and f_p is fraction of particulate.

For hydrophobic chemical such as PCBs, sorbed concentration at equilibrium is linearly related to dissolved concentration and may be written as:

$$r = K_p \times C_d \quad [10]$$

where r is the sorbed PCB mass per unit mass of sorbent (M/M) and K_p is the sorption partition coefficient (L³/M). The fractions are expressed as

$$f_d = \frac{\theta}{\theta + K_p m_w + K_{doc} m_{doc}} \quad [11]$$

$$f_p = \frac{K_p m_w}{\theta + K_p m_w + K_{doc} m_{doc}} \quad [12]$$

$$f_{doc} = \frac{K_{doc} m_{doc}}{\theta + K_p m_w + K_{doc} m_{doc}} \quad [13]$$

where m_w is suspended organic carbon concentration (M/L³)[sum of BIC and PDC], θ is porosity (water volume/total volume), and K_{doc} is the partition coefficient between PCBs sorbed to DOC and dissolved PCB (L³/M). Variable m_{doc} is the DOC concentration (M/L³).

The transfer of PCBs between sediment pore water and the water column is expressed as a diffusive process:

$$S_D = k_f (C_{ds} - C_{dw}) \quad [14]$$

where k_f is the diffusive mass transfer coefficient (L³/T), and the subscripts s and w refer to the surface sediment bed and water column, respectively.

The transport of particulate PCBs from the sediment surface to the water column via resuspension occurs at a rate that is proportional to the rate at which sediment particles are resuspended (R_s ; L/T).

The volumetric PCB flux is

$$S_R = \frac{R_s}{h_s} f_{ps} C_{Ts} \quad [15]$$

where f_{ps} is the fraction particulate in the surface sediment and variable h_s is the depth of the sediment (L).

The rate at which volatilization occurs is dependent on the mass transfer coefficient at the air-water interface and the concentration of PCBs in the water column. Only dissolved PCBs can be transported across the interface, and sorption to particulate or dissolved organic carbon reduces volatilization. The equation used to describe PCB flux due to volatilization is

$$S_V = \frac{k_V}{h} (C_d - \frac{c_{air}}{H'}) \quad [16]$$

where k_V is the volatilization mass transfer coefficient (L/T), h is the depth in the water column (L/T), c_{air} is the vapor phase PCB concentration in air (M/L³) and H' is Henry's constant (dimensionless) which is equal to the Henry constant (H in mole/m³) divided by the product of the universal gas constant (R in 0.0083143 Joules/°K·mole) and temperature (T in °K). The mass transfer coefficient is dependent on the rates of mass transfer through relatively thin layers of water and air at the interface, which are in turn dependent on the concentration gradients in the layers, and the temperature-dependent diffusivity of PCBs in the layers:

$$K_V = \frac{K_g K_L}{K_g + \frac{K_L}{H'}} \quad [17]$$

where K_g is the vapor phase mass transfer constant (L/T) and K_L is the water phase mass transfer constant (L/T).

Air-water Exchange Formulations

See section on new formulation for volatilization mass transfer coefficient (K_V).

Liquid-Film Formulations

Liquid Film coefficient (K_{L,O_2})-formulas for tidal velocity-driven functions

DELPCB incorporates Thomann and Fitzpatrick (1982) equation, which combines O'Connor-Dobbins and Banks and Herrera (1977). The idea of adopting Thomann and Fitzpatrick (1982)'s equation is that such equation provided a straight forward description of both tidal velocity and wind-driven effects for tidal systems in a continuous format. Time variable reaeration rate, K_a equals K_{L,O_2} (mass transfer coefficient of oxygen for liquid laminar layer) divided by H (mean depth). O'Connor and Dobbins 1958's equation for upper estuary and Banks and Herrera 1977's wind-base equation for windy Zone 6.

$$k_a = 3.93 \frac{\sqrt{U_0}}{H^{3/2}} + \frac{0.0728U_w^{0.5} - 0.317U_w + 0.0372U_w^2}{H} \text{ Thomann\&Fitzpatrick(1982)} \quad [18]$$

Where U_w is wind velocity (L/T), U_0 is tidal average flow velocity (L/T), k_a is reaeration rate (L/T).

K_{L,O_2} Conversion to $K_{L,PCB}$

We then convert K_{L,O_2} to $K_{L,PCB}$ (mass transfer coefficient of PCB for liquid laminar layer) via a molecular weight function described by Mills et al. (1982).

Gas-Film Formulations

Similar approach can be applied to gas-film formulations. For the gas-film coefficient of water (Kg.H₂O), Mills et al (1982) also illustrated wind-base equation. Using similar methodology, DELPCB converts such coefficient from water to gas-film coefficient of PCB (Kg.PCB).

$$K_{L.PCB} = K_{L.O_2} \left(\frac{32}{M} \right)^{0.25} \text{ Mills et al. (1982)} \quad [19]$$

Gas Film coefficient (Kg.H₂O)-formulas for wind-driven functions

$$K_{gH_2O} = 168U_w \text{ (Mills et al. 1982)} \quad [20]$$

Where U_w is wind velocity (L/T).

Kg.H₂O Conversion to Kg.PCB

Gas film water-PCB conversion using Mills et al. 1982's H₂O-PCB equations, or velocity= 100 m/day or measured

$$K_g = K_{gH_2O} \left(\frac{18}{M} \right)^{0.25} \text{ Mills et al. (1982)} \quad [21]$$

Temperature correction for Henry's Law constant

Using Bamford et al. 2002 or ten Hulscher et al. 1992 for temperature correction for Henry's Law constant

$$\begin{aligned} H_{PCB83} &= 10^{((-30.)/(0.0083143*(TMP + 273.15)))+(0.07/0.0083143)} \\ H_{PCB86} &= 10^{((-29.)/(0.0083143*(TMP + 273.15)))+(0.06/0.0083143)} \\ H_{PCB90} &= 10^{((-29.)/(0.0083143*(TMP + 273.15)))+(0.06/0.0083143)} \\ H_{PCB93} &= 10^{((-18.)/(0.0083143*(TMP + 273.15)))+(0.03/0.0083143)} \\ H_{PCB110} &= 10^{((-38.)/(0.0083143*(TMP + 273.15)))+(0.09/0.0083143)} \\ H_{PCB118} &= 10^{((-50.)/(0.0083143*(TMP + 273.15)))+(0.13/0.0083143)} \\ &\text{Bamford et al. 2002.} \end{aligned} \quad [22]$$

Where HPCB_x represents unitless HENRY's Law constant for congener x. TMP represents water temperature (°C). Weighted-based average value is used in the model.

Implementation of temporal and spatial varying Vapor Phase PCB Concentration In Air (cair)

From DRBC's Air/Water Flux study results (preliminary), cair varied from reach to reach (spatial variation) in the Delaware River with seasonal fluctuation (temporal variation). The newly developed empirical formulas for temperature dependent cair by Totten et al. 2003 have been incorporated into the model (see equation 23).

Seven APCB (unit: pg/L) formulas represent seven different cair distributions within the Delaware River Estuary (see Figure 5). ATAM(ICHM) represents scale factors which can vary both temporally and spatially. ATMP represents air temperature (°C).

3.2.2 OC Kinetic Equations

As mentioned in OC Sorbent Dynamic Section (Section 2.4.1), within surface sediment, all BIC is converted to PDC. There is no BIC in the sediment. In the water column, settling, BIC decay to PDC, and external loads are the three key players in BIC kinetic. Whereas, for PDC, in addition to settling, PDC decay to DOC, and external loads, the depositional BIC converted to PDC and resuspended PDC flux are the two important mechanisms. BIC's and PDC's kinetic equations can be expressed in the following:

3.2.3 BIC Kinetic Equations

$$\frac{\partial BIC}{\partial t} = -\frac{v_{sbic}}{h}BIC - K_{wbic}BIC + S_{BIC} \quad [24]$$

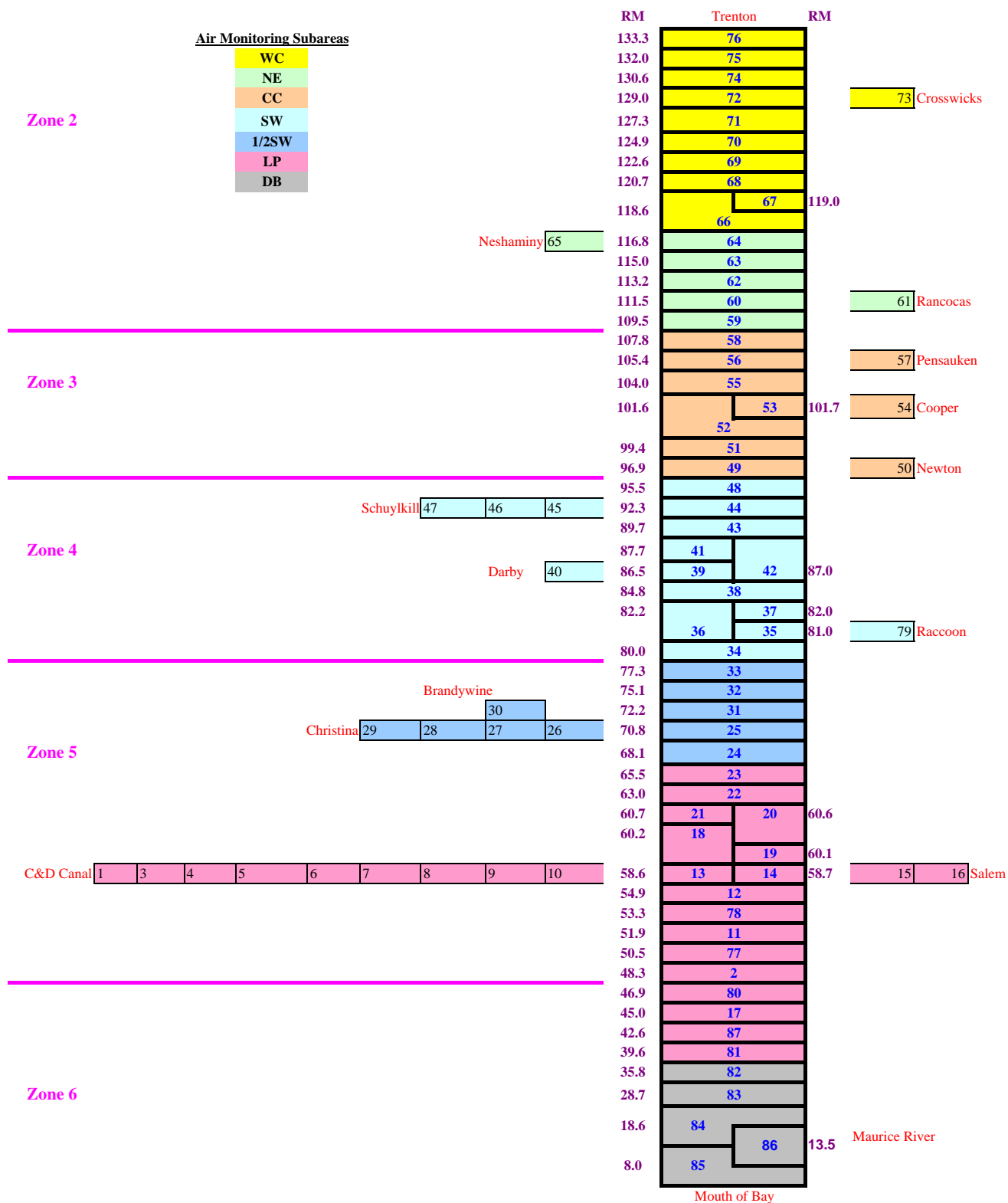
where BIC is the state variable Biotic Carbon concentration (M/L³), K_{wbic} is the BIC kinetic rate constant (1/T), and SBIC represents the external BIC loads (M/(L³ x T)).

3.2.4 PDC Kinetic Equations

$$\frac{\partial PDC}{\partial t} = -\frac{v_{spdc}}{h}PDC - K_{wpdc}PDC + K_{wbic}BIC + \frac{R_{spdc}}{h}PDC + S_{PDC} \quad [25]$$

where PDC is the state variable PDC's concentration (M/L³), K_{wpc} is PDC kinetic rate constant (1/T), R_{spdc} is the resuspension rate of PDC (1/T), and SPDC represents the external PDC loads (M/(L³ x T)).

Figure 5 - Air Monitoring Value Assignments



3.3 GOVERNING EQUATIONS FOR SEDIMENT PROCESSES

3.3.1 BALANCE EQUATIONS

3.3.1.1 PCB Mass Balance Equation

Within the sediment bed, PCBs are subject to vertical migration due to the process of mixing of particles by biological activity and water turbulence propagating into the bed, molecular diffusion within sediment pore water, and advection of water through the sediment.

The settling of PCBs from the water column to sediment is expressed as a settling process:

$$S_S = \frac{v_S}{h} f_p C_T \quad [26]$$

where v_S is the settling velocity (L/T).

Assuming that no PCB decay, the basic mass balance equation for total PCBs (i.e., the sum of dissolved, DOC-bound, and particulate-bound PCBs) in the surface sediment is

$$\frac{\partial C_T}{\partial t} = -\frac{h}{h_S} (S_D + S_R - S_S) \quad [27]$$

where h_S is depth of the surface sediment (L).

3.3.1.2 PDC and IS Mass Balance Equation

Implementation of IS in the sediment is essential because the real bulk density and porosity of the sediment must be accurately calculated at each time step so that the sediment process can be correctly simulated. IS is also an important indicator for burial rate calculations. During the sediment burying process, though no depositional IS flux from water column, model generates additional IS based on the depositional OC assuming OC/IS ratio remaining constant. These additional IS are buried with OC to maintain the same OC/IS ratio and bulk density. In the sediment, OC is solely represented by PDC. Assuming the sum of PDC and IS represents all particular matters (m) in the sediment, model can track mass balance of such particular matters. Assuming the sum of PDC and IS represents all particular matters (m) in the sediment, model can track mass balance of such particular matters. Assuming that PDC/IS ratio is η , then concentrations of PDC and IS are $m^* \eta / (\eta + 1)$ and $m / (\eta + 1)$ (M/L³). Furthermore, model generated additional IS equals $1/\eta$ of PDC flux from water column. The basic mass balance equation of particular matter which represents the sum of PDC and IS in the surface sediment can be expressed in the following:

$$m_{s1} \frac{\partial v_s}{\partial t} = A \times v_s \times PDC_w \frac{\eta+1}{\eta} - A \times R_s \times m_{s1} - A \times v_{d1} \times m_{s1} + A \times R_{s2} \times m_{s2} \quad [28]$$

Where m_s is the concentration of particulate matter in the surface sediment (M/L³), PDC_w is the concentration of PDC in the water column (M/L³), m_{s2} is the concentration of particulate matters in layer 2 sediment (M/L³), V_s is volume of surface sediment (L³), RS_1 is resuspension rate between the water column and surface sediment (L/T), vd_1 is depositional rate between layer 1 and layer 2 sediment (L/T), RS_2 is resuspension rate between layer 1 and layer 2 sediment (L/T), and A is the surface area between the water column and surface sediment (L²).

Since the constant volume bed is used for layer 2, the basic mass balance equation for particulate matters in layer 2 is slightly different from surface sediment. The equation can be expressed in the following:

$$V_{s2} \frac{\partial m_{s2}}{\partial t} = A \times v_{d1} \times m_{s1} - A \times v_{d2} \times m_{s2} + A \times v_{d1} \times m_{s1} - A \times R_{s2} \times m_{s2} + A \times R_{s3} \times m_{s3} \quad [29]$$

Where m_{s2} is the concentration of particulate matter in layer 2 sediment (M/L³), V_{s2} is volume of layer 2 sediment (L³), vd_2 is depositional rate between layer 1 and layer 2 sediment (L/T), RS_3 is resuspension rate between layer 2 and layer 3 sediment (L/T), and A is the surface area between layer 1 and layer 2 sediment (L²). Layer 3 sediment is similar to layer 2 except that there is no resuspension flux from underlying layer (the last term of the right hand side of equation).

IS is included as a pseudo-state variable in the sediment to maintain accurate bulk volume, which will be an important parameter for the long-term consistency check, while the magnitude of burial rate, changes of the bulk volume (or density) and OC/IS ratio may be an issue, if not handled properly, during the sediment processes.

To address bioturbation behavior, particle mixing and additional diffusion can be implemented between layer 1 and 2 to enhance the interactions. Based on equation 29, if we maintain the same rate of vd_2 and RS_2 , and specify variable volume option to layer 2, particle mixing will take place between layer 1 and 2. In DELPCB, we made a decision between the zero mixing and particle mixing cases (between the first two sediment layers) based on results from the long-term historical simulations. In our judgment that the dated sediment cores indicated a surface sediment layer mixed depth between approximately 5 and 10 cm.

3.3.1.3 BIC Mass Balance Equation

Upon settling to the sediment, all BIC are transformed to PDC. BIC concentration in the sediment is zero.

3.3.1.4 KINETIC EQUATIONS FOR SEDIMENT PROCESSES

Model has three state variables and one pseudo state variable. This section describes the kinetic equations for each of the state variables.

- | | |
|---------|---------|
| (1) PCB | (2) PDC |
| (3) BIC | (4) IS* |

Where * represents a pseudo state variable.

As mentioned in Section 2.4.1, there is no PCB decay and IS is deemed as a non-degradable solid due to its pseudo-state variable nature. For OC, upon settled to the sediment, all BIC are transformed to PDC. BIC concentration in the sediment is zero. Thus, there are no kinetic for these three state variables in the sediment. That leaves PDC as the sole state variable that has kinetic functions in the model

3.3.1.5 OC Kinetic Equations

The model contains only one organic carbon (PDC) in sediment. Upon settling to the sediment, all BIC turns into PDC and then is resuspended or buried. The key terms in the PDC kinetic equation include PDC settling rate, PDC decay rate, external PDC loads, depositional BIC converted to PDC and resuspended PDC flux. PDC's kinetic equation in the surface sediment can be expressed in the following:

3.3.1.6 PDC Kinetic Equations

$$\frac{\partial PDC_{s1}}{\partial t} = + \frac{v_{sbic}}{h} BIC_w + \frac{v_{spdc}}{h} PDC_w - K_{s1pdc} PDC_{s1} - v_{d1} PDC_{s1} - \frac{R_{s1}}{h_s} PDC_{s1} + \frac{R_{s2}}{h_s} PDC_{s2} \quad [30]$$

where PDCs1 is the state variable PDC's concentration in the surface sediment (M/L³), PDCs2 is the state variable PDC's concentration in layer 2 sediment (M/L³), and Kspdc is PDC kinetic rate constant in the surface sediment (1/T).

Without interactions with the settled BIC flux, the basic mass balance equation for PDC in layer 2 is slightly different from surface sediment. The equation can be expressed in the following:

$$\frac{\partial PDC_{s2}}{\partial t} = - K_{s2pdc} PDC_{s2} + v_{d1} PDC_{s1} - v_{d2} PDC_{s2} - \frac{R_{s2}}{h_s} PDC_{s2} + \frac{R_{s3}}{h_s} PDC_{s3} \quad [31]$$

where PDCs3 is the state variable PDC's concentration in layer 3 sediment (M/L³) and Ks2pdc is PDC kinetic rate constant in layer 3 sediment (1/T). Layer 3 sediment is similar to layer 2 except that there is no resuspension flux from underlying layer (the last term of the right hand side of equation).

4 SOURCE CODE VALIDATION OF DELPCB

Source code validation of DELPCB was performed and proved to be sensitive to the following test runs. The flows used for those test runs are constant so the relative responses to the changes of the selected constant or parameter are identified.

Sensitivity runs on newly added PCB partition coefficient for DOC

Sensitivity runs on whether DOC concentrations can be externally specified as spatially and temporally variable forcing functions

Sensitivity runs on whether atmospheric PCB concentrations can be externally specified as spatially and temporally variable forcing functions

Sensitivity runs on whether the conversion factor on volatilization rate is correct

Sensitivity runs on BIC and PDC loads.

The aforementioned validation results are available upon request.

Finally, the modified and newly created FORTRAN source codes for DELPCB are listed in Table 1. The newly created constants and coefficients and their associated ID in FORTRAN source codes for DELPCB are listed in Table 2. Key input parameters and values for DELPCB are shown in Table 3.

Table 1: Modified And Newly Created FORTRAN Source Codes For DELPCB

Newly Created Fortran Files	Modified Fortran Files From WASP5/TOXI5	Modified Dependencies Files From WASP5/TOXI5
SOLID	CHEM1	CHEM1.EQU
	CHEM2	CHEM2.EQU
	CHEM3	CHEM3.EQU
	CHMINT1	CHMLOC.CMN
	CHMINT2	ENVIRON.CMN
	CHMINT3	GLOBAL.EQU
	ENV	KNETIC.EQU
	FRCION	PARAM.EQU
	TOXIDU	PHYSCHM.CMN
	VOLAT	WASP.CMN
	WASPB	
	BDSER	
	QSED	

Table 2: Newly Created Constants And Coefficients And Their Associated ID in DELPCB's FORTRAN Source Codes

ID	Constants and Coefficients
1801	KHCC-HALF SATURATED CONSTANT FOR BIC IN WATER COLUMN
1802	KDCC-DECAY CONSTANT FOR BIC IN WATER COLUMN
1803	KHPP-HALF SATURATED CONSTANT FOR PDC IN WATER COLUMN
1804	KDPP1-DECAY CONSTANT FOR PDC IN WATER COLUMN
1805	LKDOC- PCB PARTITION COEFFICIENT FOR DOC FOR CHEMICAL1
1806	LKDOC- PCB PARTITION COEFFICIENT FOR DOC FOR CHEMICAL2
1807	LKDOC- PCB PARTITION COEFFICIENT FOR DOC FOR CHEMICAL3
1808	KDPP2- DECAY RATE FOR PDC IN SEDIMENT
1809	KTHC- TEMPERATURE-CORRECTED HALF SATURATION RATE FOR BIC IN WATER COLUMN
1810	KTDC- TEMPERATURE-CORRECTED DECAY RATE FOR BIC IN WATER COLUMN
1811	KTHP- TEMPERATURE-CORRECTED HALF SATURATION RATE FOR PDC IN WATER COLUMN
1812	KTDP1- TEMPERATURE-CORRECTED DECAY RATE FOR PDC IN WATER COLUMN
1813	KTDP2- TEMPERATURE-CORRECTED DECAY RATE FOR PDC IN SEDIMENT

Table 3: Input Parameters and Values for DELPCB

Parameter	Description	Value	Unit
Vd	Net deposition	1	cm/year
Vsbic	BIC Settling Velocity	0.1	m/day
Vspdc	PDC Settling Velocity	1.0	m/day
m1	Water Column Solids	0	mg/L
m2	Sediment Solids	70-120	G/L
BICw	BIC Concentration-Water	0-1.5	mg/L
BICs	BIC Concentration –Sediment	0	mg/L
PDCw	PDC Concentration-Water	0-3.5	mg/L
PDCs	PDC Concentration –Sediment	8000-22000	mg/L
Kdbicw	BIC Decay rate-Water	0.2	1/day
Kdbics	BIC Decay rate- Sediment	0	1/day
Kdpdcw	PDC Decay rate-Water	0.05	1/day
Kdpdcs	PDC Decay rate- Sediment	0.00026	1/day
DOCw	Dissolved organic carbon-water column	4 - 9	mg/L
DOCs	Dissolved organic carbon-Sediment	10	mg/L
Koc	Partition Coefficient- organic carbon	6.26	logL/kg
Kdoc	Partition Coefficient-DOC	5.26	logL/kg
Kv	Air-water exchange rate in water column	-1.0-0.5	1/day
Kd	PCB Decay rate	0	1/day
El	Longitudinal dispersion coefficient	0 -250	m2/sec
Ev	Vertical diffusivity b/w water column/sediment	1.00E-10 1.00E-08	m2/sec
Wcln	EPA superfund site loadings	DEL/EPA report	kg/day
Wnps	NPS loadings	CDM report	kg/day
Wt	Tributary loadings	DRBC report	kg/day
Weso	CSO loadings	DRBC report	kg/day
As/w	Surface area b/w water column/sediment	DYNHYD5	m2
Vs/w	Volume/sediment	DYNHYD5	m3
Aw	Surface area-water column	DYNHYD5	m2
Vw	Volume/water column	DYNHYD5	m3

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APPENDIX

DISCUSSIONS ON CODE MODIFICATIONS TO WASP5/TOXI5

A. DISCUSSIONS ON CODE MODIFICATIONS TO WASP5/TOXI5

DELPCB models PCB, two classes organic carbons, and one inorganic solid. The distribution of PCB between the dissolved and various particulate phases is computed from the total PCB assuming instantaneous equilibrium linear partitioning. Up to three PCB homologs can be modeled. In our study, SYSTEM 1 is PCB; SYSTEMS 2 and 3 are BIC and PDC, respectively; SYSTEMS 4 is inorganic SOLID and SYSTEMS 5 and 6 are not being used.

DELPCB has the capacity to incorporate the following algorithms which are not included in the original WASP5/TOXI5:

A.1 A DIFFERENT VALUE SHOULD BE ASSIGNED TO PCB PARTITIONING COEFFICIENT DOC (KDOC)

In standard TOXI5, there is only one PCB partitioning coefficient to OC (Koc) but no other value can be assigned to PCB partitioning coefficient DOC (Kdoc). As indicated in the literature, binding capacity of PCBs with POC is greater than that observed with DOC in Great Lakes waters (i.e., Koc is greater than Kdoc) (Gilek et al., 1996) (Strange and Swackhamer, 1994) (as referred to as Chapra, 1997). It is suggested by PCB modeling expert panel that a value of Kdoc that is 10 percent of the value for Koc.

The following is how such a modification works.

First, initiate and establish two different constants for Koc and Kdoc in CHEM1.FOR. Realizing the hydrophobic nature of PCB, the 10 base exponential functions are implemented to both Koc and Kdoc.

```
      XARG=ABS(LKOC)
      IF (XARG .LT. R0MIN) THEN
        KOC = 0.0
      ELSE
        KOC = 10**LKOC
      END IF
      XARG=ABS(LKDOC)
      IF (XARG .LT. R0MIN) THEN
        XDOC=0.0
      ELSE
        XDOC = 10**LKDOC
      END IF
```

Second, based on equations 11 through 13, model calculates the PCB distributions between BIC, PDC, DOC, and truly dissolved phases; and route through their associated flow fields to complete the partitioning processes. As an example, the following code is retrieved from Frcion.FOR for illustration purpose.

```
C   I. COMPUTE DISTRIBUTION FACTORS FOR EACH PHASE AND SPECIE
C     Distribution factor is the ratio of component concentration
```

```

C      to dissolved parent compound concentration
C      A) SORBED TO SOLIDS:
      IF (ICHM .EQ. 1) JS = 1
      IF (ICHM .EQ. 2) JS = 5
      IF (ICHM .EQ. 3) JS = 6
      DO 1000 J = 1, 3
        JJ = 5*(J - 1)
        SLD = C(J+1,ISEG)*1.0E-06
C      1) parent compound
        DISFCT (1 + JJ) = PART (J, 1)*SLD
1000 CONTINUE
C      B) SORBED TO DOC:
      DOCKGL = SDOC*1.E-06
C      1) parent compound
      DISFCT (16) = XDOC*DOCKGL
C      C) DISSOLVED:
C      1) parent compound
      DISFCT (21) = 1. * PORE
C      II. COMPUTE FRACTION OF TOTAL CHEMICAL FOR EACH COMPONENT
C      A) SUM DISTRIBUTION FACTORS
      DENOM = 0.0
      DO 1010 K = 1, 25
C      For doc sorbed & dissolved components multiply by
C      porosity to convert water volume to total volume
        DENOM = DENOM + DISFCT (K)
1010 CONTINUE
C      B) COMPUTE FRACTIONS
      DO 1020 K = 1, 25
        FRAC (K) = DISFCT (K)/DENOM
        IF (FRAC (K) .LT. 1.00E-10) FRAC (K) = 0.0
1020 CONTINUE
C      C) COMPUTE COMPONENT CONCENTRATIONS
C      1) solids sorbed components
      k=0
      DO 1030 J = 1, 3
        DO 1040 ION = 1, 5
          K = K + 1
          PARTOX (ICHM, J, ION) = FRAC (K)*C (JS, ISEG)
          IF (PARTOX (ICHM, J, ION) .LT. 1.0E-30)
            1 PARTOX (ICHM, J, ION) = 0.0
1040 CONTINUE
1030 CONTINUE
C      2) doc sorbed components
      DO 1050 K = 16, 20
        DOCTOX (ICHM, K - 15) = FRAC (K)*C (JS, ISEG)
        IF (DOCTOX (ICHM, K - 15) .LT. 1.0E-30)
          1 DOCTOX (ICHM, K - 15) = 0.0
1050 CONTINUE

```

```

C      3) dissolved components
      DO 1060 K = 21, 25
        DISTOX (ICHM, K - 20) = FRAC (K)*C (JS, ISEG)
        IF (DISTOX (ICHM, K - 20) .LT. 1.0E-30)
          1    DISTOX (ICHM, K - 20) = 0.0
      1060 CONTINUE
C      D) EQUATE FRACTIONS TO F ARRAY FOR PROPER TRANSPORT
C      NOTE: The transport (exchange & flow) fields must
C      be as follows:
C      field #1 applies to total chemical
C      field #2 applies to dissolved & doc sorbed chemic
C      field #3 to field N applies to particulate chemic
      F (1, JS, ISEG) = 1.0
      F (2, JS, ISEG) = 0.0
      DO 1070 K = 16, 25
        F (2, JS, ISEG) = F (2, JS, ISEG) + FRAC (K)
      1070 CONTINUE
      K=0
      DO 1080 J = 1, 3
        F (J + 2, JS, ISEG) = 0.0
        DO 1090 ION = 1, 5
          K = K + 1
          F (J + 2, JS, ISEG) = F (J + 2, JS, ISEG) + FRAC (K)
        1090 CONTINUE
      1080 CONTINUE
      RETURN
      END

```


A.2 ENHANCEMENT OF DOC'S TEMPORAL FLEXIBILITY

Upon examining standard TOXI5's input options DOC can be incorporated as spatial variables in Group G: Parameter but is not a temporal variable. To better track of organic carbon balance, we need to enhance the temporal flexibility of DOC.

The following is how such modification works.

$$1005 \text{ SDOC} = \text{DOC (ISEG)} * \text{DOCN from ENVIRON.FOR}$$

Existing spatial function DOC (ISEG) is linked with newly created time function (temporal varying) DOCN to form both spatial and temporal varying SDOC. SDOC enhances of DOC's temporal flexibility.

A.3 DEGRADABLE ORGANIC CARBONS FOR BOTH WATER COLUMN AND SEDIMENT

As mentioned in Section 2.3.1, TOXI5 treats the three organic carbons as conservative constituents that are advected and dispersed among water segments, that settle to and erode from benthic segments, and move between benthic segments through net sedimentation or erosion. To develop a good OC sorbent dynamic model, decay rates need to be applied to both BIC and PDC. Such a OCSD model should apply water column gross settling and decay functions to describe physical and biological processes for BIC and PDC. Within water column, BIC is converted to PDC and then, together with PCB, transformed into DOC. Upon settling to the sediment, all BIC turns into PDC and then resuspended or buried.. For sediment processes, to fulfill the second basic process which is the diagenesis of depositional OC flux a sediment OC decay function is required.

The following is how such a modification works.

First, initiate and establish carbon related constants

KDCC decay rate for BIC

KDPP1 decay rate for PDC in water column

KDPP2 decay rate for PDC in sediment

KTHC temperature-corrected half saturation rate for BIC

KTDC temperature-corrected decay rate for BIC

KTDP1 temperature-corrected decay rate for PDC in water column

KTDP2 temperature-corrected decay rate for PDC in sediment

Second, link these constant with temporal and spatial varying water temperature function for temperature correction (to address the seasonal kinetic behavior).

Third, based on equations 24, 25, 30, and 31, model calculates the kinetic part of OC sorbent dynamic for BIC and PDC; and routes through their associated flow fields to complete the kinetic processes.

Fourth, to incorporate the sediment processes for PDC and IS described in equations 28 and 29, subroutine BEDSED.FOR and QSED.FOR need modifications to ensure (1) conversion of BIC to PDC (BIC concentration in the sediment is zero), (2) same OC/IS ratio and bulk density is maintained [in variable bed volume option, it also indicates both PDC and IS concentrations remain constant], (3) additional IS is generated based on the depositional OC based on a constant OC/IS ratio, and (4) sediment burial for both IS and PDC function properly. The sum of IS and OC (or PDC) burial rate computed by DELPCB represents sediment burial rate and is compared with sediment core data.

As an example, the following code is retrieved from Solid.FOR. Such subroutine has been extensive upgraded and is very different from the original TOXI5. The innovative modifications of subroutine BEDSED.FOR and QSED.FOR are also included.

Subroutine Solid.FOR

```
C  B) DEFINE F ARRAY FOR PROPER TRANSPORT
DO 1010 J = 2, 4
  F (1, J, ISEG) = 1.0
  F (2, J, ISEG) = 0.0
  F (J + 1, J, ISEG) = 1.0
1010 CONTINUE
  XARG=ABS(CD (J,ISEG))
  IF (XARG .LT. R0MIN) THEN
    DO 100 J=2,4
      CD (J, ISEG)=0.0
100 CONTINUE
    ELSE
    ENDIF
    IF (ITYPE(ISEG) .EQ. 1) THEN
      XARG=ABS(KDC)
      IF (XARG .NE. 0.0) THEN
        CD (2, ISEG) = - (KDC)*C (2, ISEG)
      ENDIF
      XARG1=ABS(KDP1)
      IF (XARG1 .NE. 0.0) THEN
        XARG=ABS(KDC)
        IF (XARG .NE. 0.0) THEN
          CD (3, ISEG) = -(KDP1)*C (3, ISEG)+
1          (KDC)*C (2, ISEG)
        ELSE
          CD (3, ISEG) = - (KDP1)*C (3, ISEG)
        ENDIF
      ELSEIF (XARG .NE. 0.0) THEN
        CD (3, ISEG) = (KDC)*C (2, ISEG)
      ENDIF
    DO 101 J=2,4
      CD (J, ISEG) = CD (J, ISEG)*BVOL (ISEG)
101 CONTINUE

    ELSEIF (ITYPE(ISEG) .GT. 1) THEN
      CD (3, ISEG) = - (KDP2)*C (3, ISEG)
    DO 102 J=2,4
      CD (J, ISEG) = CD (J, ISEG)*BVOL (ISEG)
102 CONTINUE
```

Subroutine BEDSED.FOR

```
IF (ISYS .EQ. 4) THEN
  CD(4,ISEG) = CD(3,ISEG)*C(4,ISEG)/C(3,ISEG)
END IF
```

Subroutine QSED.FOR

```
IF (I .GT. 0) THEN
  IF (ISYS .NE. 2) THEN
    CD (ISYS, I) = CD (ISYS, I) + Q*CSTAR
  ELSE
    CD (3, I) = CD (3, I) + Q*CSTAR
  END IF
END IF
```

A.4 IMPLEMENTATION OF TEMPORAL AND SPATIAL VARYING VAPOR PHASE PCB CONCENTRATION IN AIR (CAIR)

Vapor phase PCB concentration in air (cair), expressed in term of atmospheric PCB concentration (ATMOS) in TOXI5, is programmed as a constant, which is neither spatially nor temporally variable. From DRBC's Air/Water Flux study results (preliminary), cair varied from reach to reach (spatial variation) in the Delaware River with (temporal variation). To better describe the field conditions in the river, we need to modify current standard TOXI5 for cair accordingly. A newly developed empirical formula for temperature dependent cair by Totten et al. 2003 was incorporated into the model.

The following is how such a modification works.

Atmospheric PCB concentrations are externally specified as spatially and temporally variable forcing functions. To achieve such, three time functions (ATMN1, ATMN2, ATMN3) and three parameters (ATM1, ATM2, and ATM3) are linked with an assigned variable ATAM(ICHM). Spatially and temporally variable atmospheric PCB (APCB) concentrations are achieved by adding air-temperature dependent functions described in equations 23 (as part of Volat.FOR expressed in FORTRAN coding style), which allows space varying input of atmospheric PCB concentrations.

A.5 IMPLEMENTATION OF TEMPERATURE-DEPENDENT CONGENER-SPECIFIC DIMENSIONLESS HENRY'S CONSTANT (H')

Congener-specific Henry's (H) constants reported by Dunnivant et al, 1992 was used to calculate Henry's constant for each PCB homolog. After applying Gas Law conversion factors, the value for the dimensionless Henry's constant (H') for each PCB homolog was calculated. For each homolog, H' and molecular weight was calculated by assuming equal weight of congener distribution. A newly developed empirical formula for temperature dependent H' by Bamford et al. 2002 is incorporated into the model.

The following is how such a modification works.

Dimensionless Henry's constant (H') for penta PCB is programmed in water-temperature dependent functions described in equations 22 (as part of Subroutine CHEM1.FOR expressed in FORTRAN coding style). Bamford et al. 2002 also listed formulas for other PCB homologs, which will be useful for the future upgrade of the model.

A.6 NEW FORMULATION FOR VOLATILIZATION MASS TRANSFER COEFFICIENT (KV)

The mass transfer coefficient is dependent on the rates of mass transfer through relatively thin layers of water and air at the interface, which are in turn dependent on the concentration gradients in the layers, and the temperature-dependent diffusivity of PCBs in the layers: In TOXI5, kV can be both temporally and spatially variable by using the combination of volatilization option 4 for XV, multiplier of time function 5, REAER, and time variable reaeration coefficient, REARN as well as air temperature, AIRTMPN to get Ka (reaeration rate). A good air-water formulation for the estuary should include both tidal velocity and wind-driven effects for tidal systems. We have reviewed the tidal velocity formulas, e.g., O'Connor-Dobbins (1958), Churchill (1962), Ovens-Gibbs (1964) for streams and rivers; and wind-driven effects, e.g., Broecker et al. (1978), Wanninkhof et al. (1991), Banks and Herrera (1977), and O'Connor (1983) for lakes. DELPCB incorporates Thomann and Fitzpatrick (1982) equation, which combines O'Connor-Dobbins and Banks and Herrera (1977). The idea of adopting Thomann and Fitzpatrick (1982)'s equation is that such an equation provides a straight forward description of both tidal velocity and wind-driven effects for tidal systems in a continuous format. The temporally varying reaeration rate, Ka equals KL.O2 (mass transfer coefficient of oxygen for liquid laminar layer) divided by H (mean depth). We then convert, KL.O2 to KL.PCB (mass transfer coefficient of PCB for liquid laminar layer) via a molecular weight function described by Mills et al. (1982). For the gas-film coefficient of water (Kg.H2O), Mills et al (1982) also illustrated a wind-base equation. A similar approach can be applied to covert such coefficient from water to PCB.

The following is how such a modification works.

The aforementioned formulas for two-film air-water exchanged have been incorporated into DELPCB. These formulas are detailed in equations 18 through 21. As programmed in subroutine Volat.FOR, upon obtaining KL.O2 and Kg.H2O, these values are then converted to KL.PCB (XKL) and Kg.PCB (XKGH), respectively. Kv is calculated based on equation 17 and then followed with temperature correction functions to become KL. With the air-water exchange rate, model calculates the Sv (air-water exchange flux) based on equation 16. The unit conversion for these detailed formulations has been properly executed. Specifically, the units for model input Cair is pg/L or slope and formula that converted to pg/L. VLT is in a unit of 1/day, which can be converted to ng/(m2.day) while divided by water depth.

SOBROUTINE VOLAT.FOR

```

XKL = (3.93*(VEL**0.5)/(SDEPTH**1.5) +
      + (0.728*(SWIND**0.5)-0.317*SWIND+
+ 0.0372*(SWIND**2.)/SDEPTH))*((32/MOLWT)**0.25)*SDEPTH
XKGH = 168.*SWIND*((18./MOLWT)**0.25)
KL = (1./(1./XKL + 1./XKGH))*KLT**STP20
KLA = KL/SDEPTH

```

$$\text{VLT(ICHM)} = \text{KLA} * (\text{DISTOX (ICHM, 1)} - \text{APCB(ICHM)}) / \text{KAW}$$